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Feasibility of Anodic Coatings on Al₂O₃ Fiber-Reinforced Aluminum Metal Matrix Composites for Wear and Corrosion Resistance

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14. ABSTRACT Aluminum and its alloys exposed to air are protected by a native oxide film that is heterogeneous in nature and does not provide adequate corrosion resistance. For this reason, anodized coatings are often used for corrosion as well as wear protection on aluminum alloys. While there is a wealth of information available about the effectiveness of anodized coatings on aluminum and aluminum alloys, little can be found about the coatings' effectiveness on aluminum matrix composites. Metal matrix composites, in general, offer new challenges in corrosion protection. Depending on the fiber material, galvanic reactions can occur at the fiber/matrix interface that could accelerate the corrosion process. Fiber "pull-out" can also affect the surface by leaving behind crevices that can also lead to preferential corrosion sites. The object of this study was to investigate the effectiveness of a type III anodic hardcoat on a 3M NEXTEL (Al ₂ O ₃) fiber-reinforced aluminum matrix composite. The corrosion and wear properties are presented and compared with an anodized monolithic baseline.					
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1. Introduction

The U.S. Army is continually seeking to lighten its force in an effort to increase mobility, deployability, and lethality. For this reason, the potential use of metal matrix composites (MMCs), specifically aluminum matrix fiber-reinforced composites, is coming more to the forefront. Fiber reinforcement of aluminum alloys offers a higher strength-to-weight ratio, stiffness, and modulus (*E*), making them ideal candidates for many U.S. Army applications. One such application is for use in advanced artillery projectiles. MMCs are being looked at for shell bodies that are 50% lighter than steel shells, allowing more payload to be carried for a given weight and volume (2). But MMCs can introduce new challenges in field applications. Corrosion protection is a prominent issue with many of the U.S. Army's systems, and replacing monolithic materials with MMCs can complicate matters further. For example, depending on the fiber material, galvanic reactions can occur at the interface of the two materials which would accelerate the corrosion process. Also, fiber "pull-out" at the surface will leave behind a void or (crevice) that also creates a region of preferential corrosion. Therefore, a coating is usually necessary for corrosion protection. Currently, the U.S. Army requires a type III hardcoat anodizing per MIL-A-8625F (3) on all aluminum ordnance shells.

The two primary objects of this study are as follows: (1) To investigate the effectiveness of a type III anodic hardcoat on a 3M NEXTEL fiber-reinforced aluminum matrix composite relative to the baseline type III anodic hardcoat on monolithic aluminum 6061 and (2) to determine if an aluminum-rich outer layer is necessary to form an effective anodic coating. Aluminum and its alloys exposed to air are already protected by a native oxide film. However, this layer is heterogeneous in nature and does not provide adequate corrosion resistance (4). Anodizing can be viewed as a deliberate controlled corrosion of an aluminum surface to create (grow) a uniform, continuous protective oxide film (5). This can be achieved using several types of electrolyte baths including chromic and sulfuric acid. Type III coatings are generally thought of as wear-resistant coatings. However, the corrosion resistance can be enhanced by using various coatings and sealers. While there is an abundance of available information about the effectiveness of anodic coatings on aluminum and aluminum alloys, little can be found about the process and effectiveness of anodic coatings on aluminum matrix composites.

What is known is that, on monolithic aluminum, an anodic coating consists of a thin continuous barrier layer beneath a thicker porous columnar-structured layer. This porous layer has been characterized elsewhere (5, 6) as a closed packed array of columnar hexagonal cells that contain a central pore. The columns are oriented normal to the substrate surface (figure 1). The concern is whether an anodic coating as described can adequately be formed on the surface of an aluminum matrix composite. And if not, will the anodization of the exposed matrix material be enough to provide adequate corrosion and wear protection to satisfy the specification?

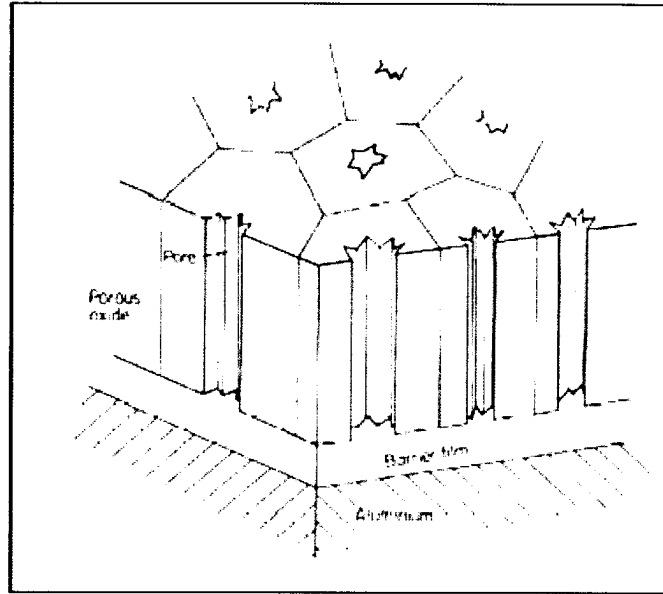


Figure 1. An accepted schematic of an anodic film structure derived from metallographic investigation (5).

2. Experimental Procedure

2.1 Specimen Preparation

All substrate material was supplied by 3M Corporation. MMC coupons were manufactured using 3M proprietary NEXTEL fibers. Because of the cost of the MMC material, it was purchased in limited supply. Thus, to maximize the amount of samples available for testing, they were machined by 3M to the geometry shown in figure 2. Five samples of each were prepared as listed in table 1. Monolithic aluminum 6061 matrix material samples were also supplied by 3M and included in the test matrix as the anodized baseline comparison.

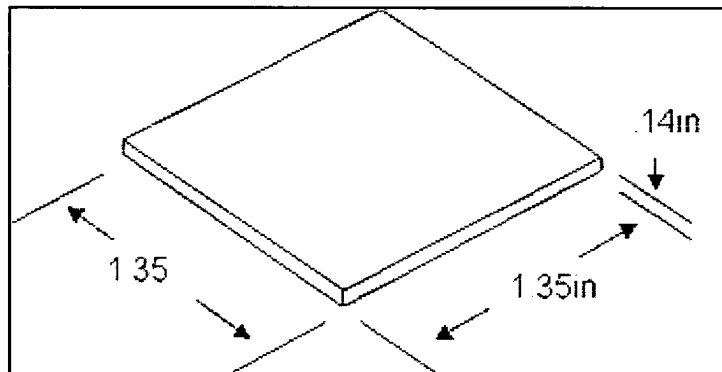


Figure 2. Specimen geometry of both monolithic and NEXTEL MMC coupons.

Table 1. List of data set identification along with the treatment conditions tested.

Description of Data Set Identifications		
Data Set ID	Substrate Material	Anodization Treatment
A1 DT3	Monolithic aluminum 6061	Deoxidized/type III/HWS
A1 NT	Monolithic aluminum 6061	No treatment
A1 DT3	Monolithic aluminum 6061	Deoxidized/type III/no seal
MMC DT3s	MMC	Deoxidized/type III/HWS
MMC IDT3	MMC	IVD coated/deoxidized/type III/no seal
MMC IDT3s	MMC	IVD coated/deoxidized/type III/HWS
MMC T3s	MMC	Type III/HWS
MMC IVD	MMC	IVD only
MMC DT3	MMC	Deoxidized/type III/no seal
MMC T3	MMC	Type III/no seal
MMC NT	MMC	No treatment

Notes: HWS = hot water seal, and IVD = ion vapor deposition.

Some MMC coupons were coated with a thin layer of pure aluminum using an IVD process. The IVD was a class I, deposited at 1/4 A and 600–700 V. Four passes were made for a final thickness of ~0.0005 in. Anodized samples were prepared according to MIL-A-8625F using a sulfuric acid anodizing process and type III hardcoat anodized to an average thickness of ~0.002 in. The anodizing is a four-step process that includes (1) degreasing, (2) deoxidizing, (3) anodizing, and (4) sealing. First, all coupons were degreased using acetone. Then, to remove the native oxide layer on the coupons, deoxidizing was performed at room temperature using an ISO McDermot solution (7). The anodizing was done as a type III in sulfuric acid, starting at 0 V, and ramping up to 24–26 V over 3 min. The deionized HWS was performed at 95 °F for 15 min.

2.2 Electrochemical Evaluation

Electrochemical impedance spectroscopy (EIS) was employed to measure coating integrity over time. The apparatus used consisted of a Princeton Applied Research (PAR) Model 283 potentiostat, a Schlumberger Model 1255 frequency response analyzer (FRA), and a Panasonic Model CF-71 laptop computer. Periodic measurements were taken at 0, 24, 48, 72, 144, 168, 336, 504, 720, and 1008 hr of continuous exposure using the cell configuration illustrated in figure 3. The cell was filled with 25 mL of 0.5-N NaCl solution and allowed to equilibrate for at least 3 hr prior to taking measurements. The software package Zplot was used for data acquisition, and Zview for data analysis. Measurements were taken at the corrosion potential of the sample over the frequency range of 100 kHz–0.01Hz. The single sine technique was utilized, with an applied amplitude of 5 mV.

The EIS data were plotted and evaluated in Bode and Nyquist formats. The Bode formats display the magnitude ($\log |Z|$) and phase angle (θ) of the impedance as a function of applied frequency

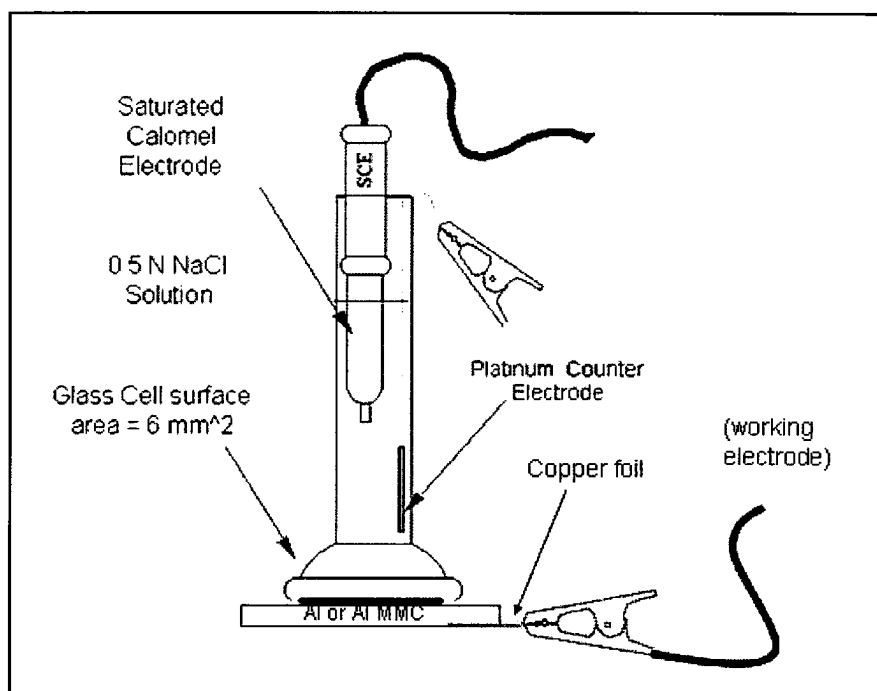


Figure 3. Electrochemical corrosion cell configuration used for alternating current impedance measurements.

(log f). The total impedance of the specimen, defined as the $\log |Z|$ value at 10 mHz in the Bode magnitude plot, was also plotted as a function of exposure time for comparison.

2.3 Abrasion Resistance

The relative wear resistance of each specimen was measured using the ball-on-disc technique. The system consisted of an Implant Sciences Corp ISC-200 tribometer and a computer interface data acquisition unit, PC-Stripchart, which is a computer-based chart recorder used to display and store data in real time.

The samples were mounted on the top of a rotating platform of the tribometer (figure 4). A 0.5-in stainless steel ball is attached to a precision balanced lever arm and is used to both apply vertical loads to the ball and to read the friction force on the pin. The ball is put in contact with the surface of the sample, and a load is applied. To measure the friction coefficient of the sample, the load was set to 100 g (a load of $\sim 1 \text{ N}$). The sample is then rotated, and the total distance the steel ball travels on the sample is set. In this case, the total distance traveled was 1000 m. All the friction measurements were conducted dry (without lubrication). Finally, the groove depth was measured using a Taylor-Hobson laser profilometer.

2.4 Accelerated Corrosion Testing

Salt fog testing in accordance with ASTM B 117 (8) was used to evaluate the corrosion resistance of the anodized coatings. The samples were placed into the salt fog chamber for a



Figure 4. Ball-on-disc tribometer test apparatus which also includes a PC for data acquisition.

total duration of 1100 hr. The samples were periodically removed for observation and were photographed at 24-, 48-, 144-, 216-, 336-, 504-, 811-, 1100-hr intervals.

3. Results and Discussion

EIS was used to measure the dielectric response of the coating as it degraded over the 30 days of immersion in 0.5-N sodium chloride (NaCl) solution. A total of eight low-frequency impedance measurements were recorded for each sample over the 30 days and plotted as a function of exposure time in figure 5. As expected, both the sealed and unsealed anodized monolithic 6061 maintained the highest impedance values throughout the 30 days exposure. In fact, all samples with the exception of bare aluminum (Al NT) remained relatively flat with no significant change in impedance. However, figure 5 shows little evidence that a sealed anodized coating provides better wet electrical resistance than unsealed on MMC. This is likely because of the surface roughness and protruding fibers present at the surface of the samples that cause pathways for the electrolyte to penetrate the coating.

Evidence of the corrosion performance can be seen in the results of the ASTM B117 salt fog testing (figures 6–8). The minimum required exposure to ASTM B117 salt fog chamber, according to MIL-A-8625, is 336 hr. It is evident in figure 8 that the baseline, Al 6061 type III HWS, reacted as expected, outperforming all others beyond the 336-hr minimum. However, the MMC type III HWS was adequately corrosion resistant up to 336 hr of B117 exposure. Beyond that, significant degradation is observed. Figure 7 shows the results at 1000 hr. Figure 7 illustrates the effects of three different scenarios on each of the substrate materials at 336 hr of B117 salt fog exposure. Here, it can be seen that the anodic coating alone provided some corrosion protection to the MMC. By including an HWS, the corrosion resistance of the anodic coating is enhanced further.

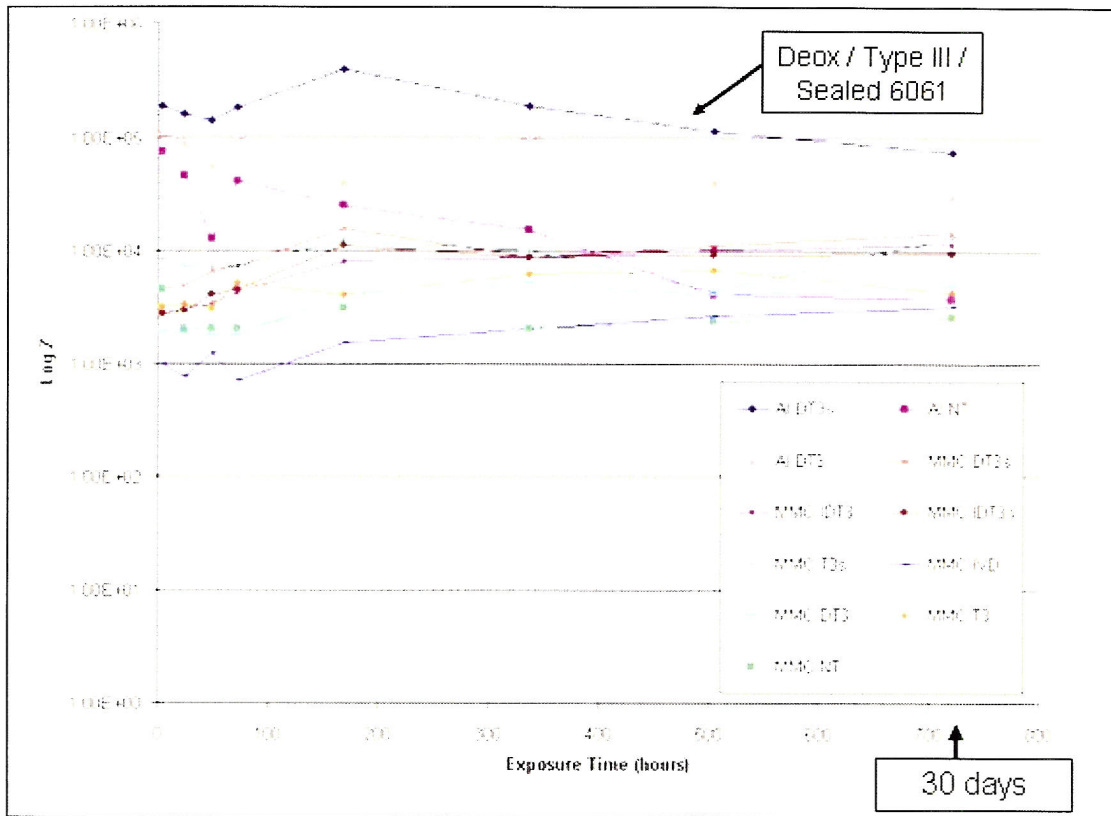


Figure 5. Low-frequency impedance vs. exposure time in 0.5-N NaCl.

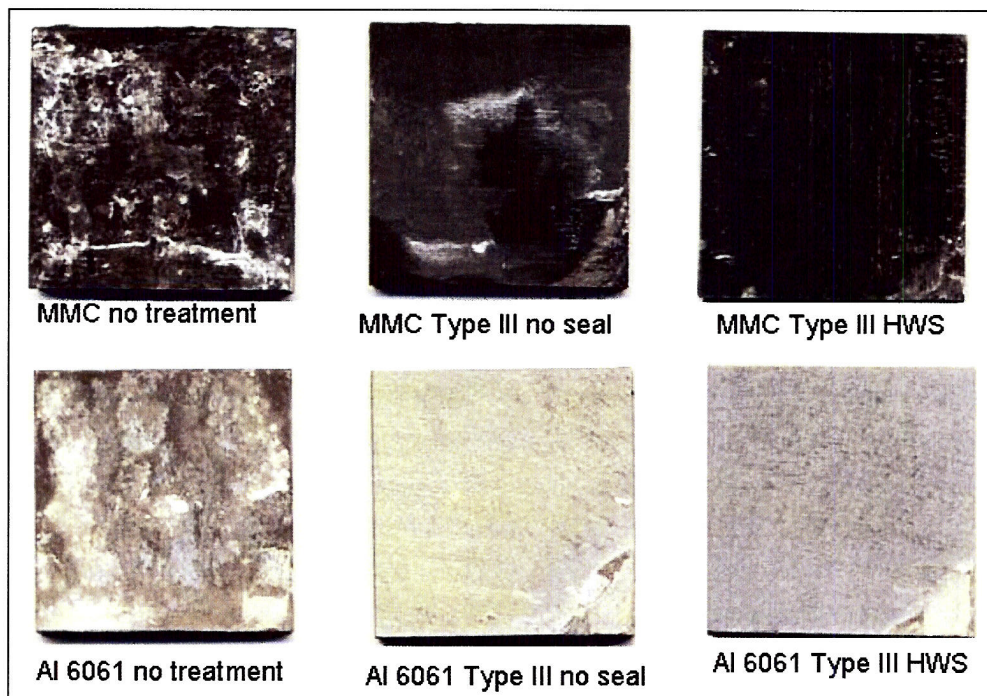


Figure 6. A comparison of three treatment scenarios for each substrate material after 336 hr of B117 salt fog exposure.

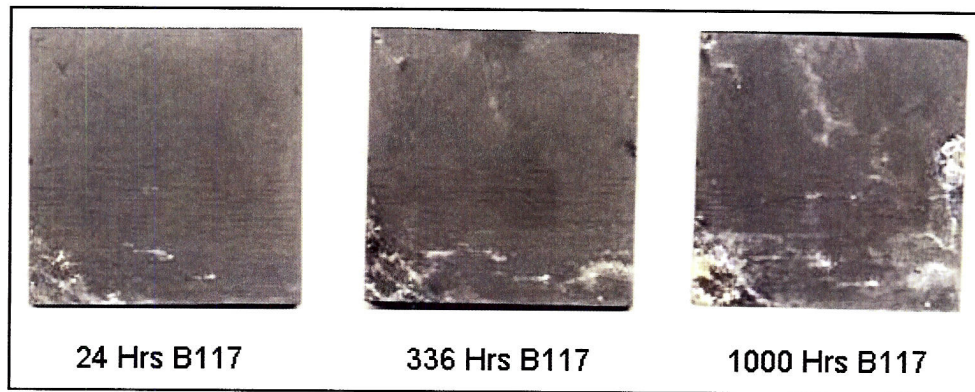


Figure 7. B117 exposure results of the IVD aluminum-coated, anodized, and sealed MMC samples.

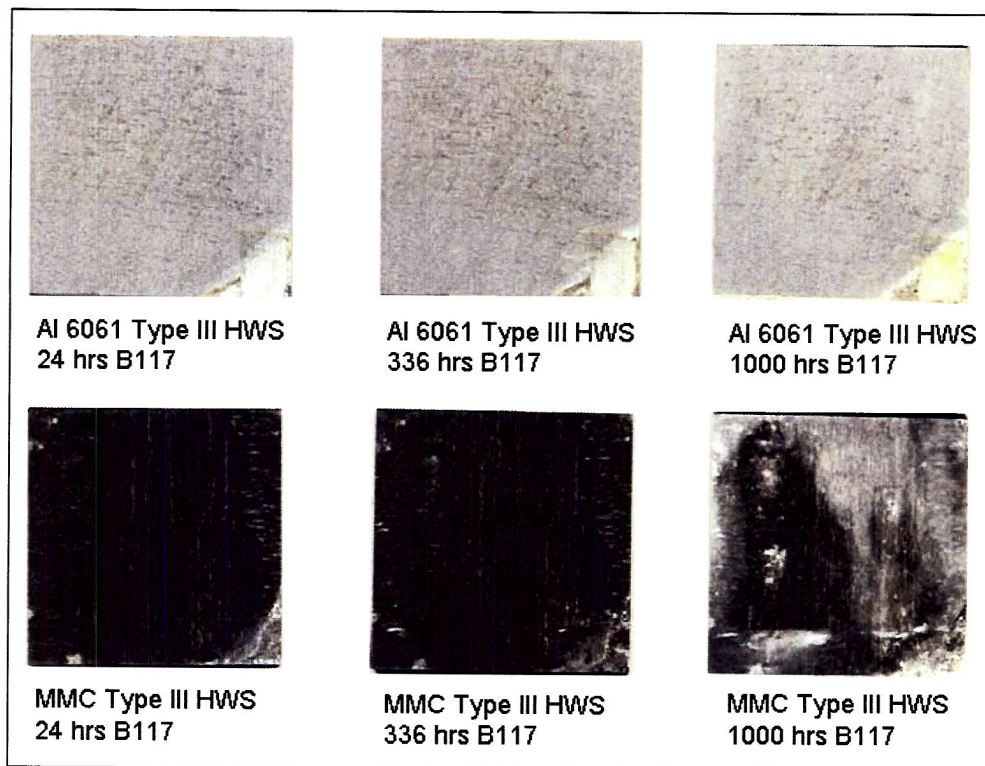


Figure 8. Comparison of Al 6061 vs. MMC over a range of salt fog exposure. The 336-hr duration represents the minimum requirement of MIL-A-8625F.

As mentioned earlier, a thin coating of aluminum, though porous, provided some corrosion protection for the MMC samples. Figure 7 illustrates the level of corrosion protection provided by the IVD aluminum, anodized, and sealed coating. When compared to the anodized and sealed MMC sample in figure 8, the IVD coated, anodized, and sealed performed comparably at 336 hr and considerably better at 1000 hr. Scanning electron microscopy (SEM) was used in order to ascertain the quality of the coatings as well as measure the coating thicknesses. A comparison of the coated monolithic samples and the MMC samples is made in figures 9 and 10. As can be

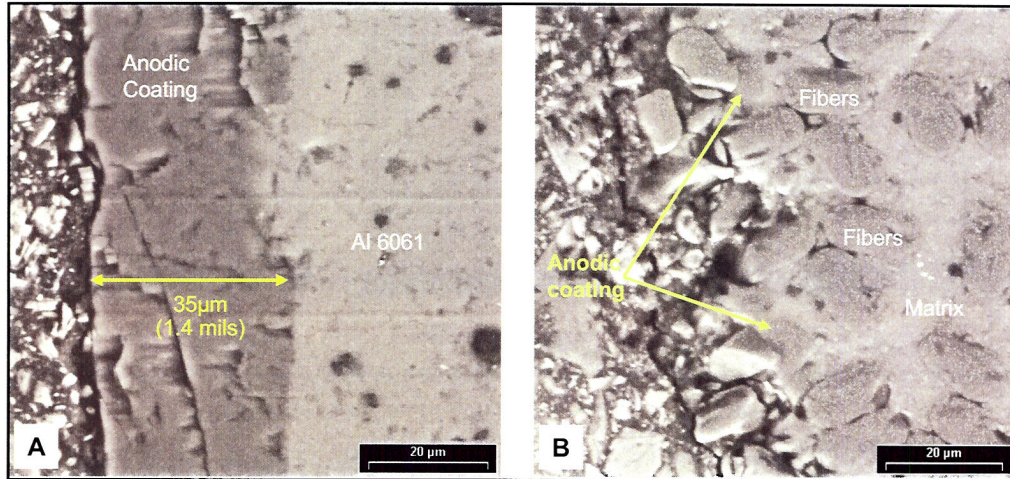


Figure 9. Cross section of type III anodized and HWS: (a) monolithic 6061 aluminum alloy and (b) aluminum matrix composite substrate.

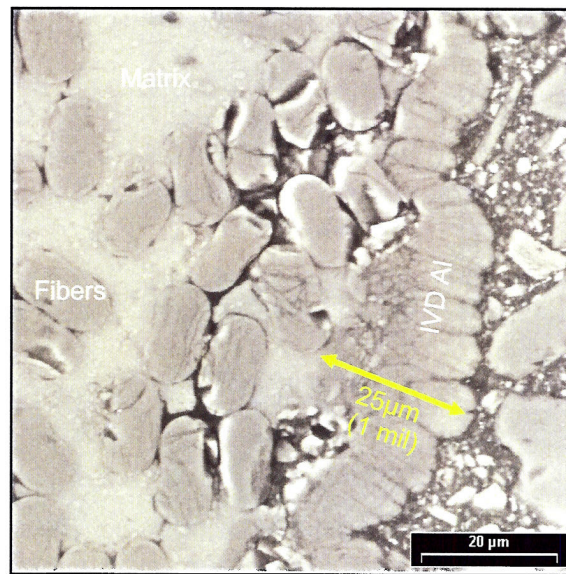


Figure 10. Aluminum matrix composite substrate with a precoating of IVD aluminum then type III anodized and hot water sealed.

seen in figure 9a, a relatively dense coating is achieved on the anodized monolithic sample. No gaps or voids were observed at the coating/substrate interface indicating that good adhesion was also probable on this sample. Although the thickness of the coating achieved, 0.0014 in (35 µm), was somewhat less than the target thickness of 0.002 in (50.8 µm), it is significantly thicker than what was realized on the MMC sample (figure 9b). It's likely that the NEXTEL fibers at or near the surface of the sample hindered the growth of the anodic coating on the MMC. The thickness of the anodic coating on bare MMC was on ~0.0002–0.0003 in (5–8 µm) thick, nearly an order of magnitude less than the target thickness of 0.002 in. When the MMC is coated with a thin layer

of aluminum, it becomes a slightly better candidate for anodization. The process of IVD leaves behind a rather porous coating. This can clearly be seen in figure 10 where the porosity appears to be continuous in some places even after anodizing. The anodizing of the porous coating appears to penetrate beyond the aluminum coating and into parts of the aluminum matrix. When sealed, the anodized IVD becomes an adequately corrosion-resistant coating.

The relative abrasion resistance was measured using a ball-on-disc tribometer. The depth of groove for each coating scenario was recorded and presented in figure 11. Using the monolithic samples as a baseline, it can be seen that the bare sample suffered the most wear in this set. When anodized, a significant increase in wear resistance is achieved. However, sealing the anodic coating reduced the wear properties slightly. This was expected, as type III coatings typically are left unsealed when the main function of application is to obtain the maximum degree of abrasion or wear resistance (3). Sealing to improve the corrosion resistance will diminish the wear resistance slightly.

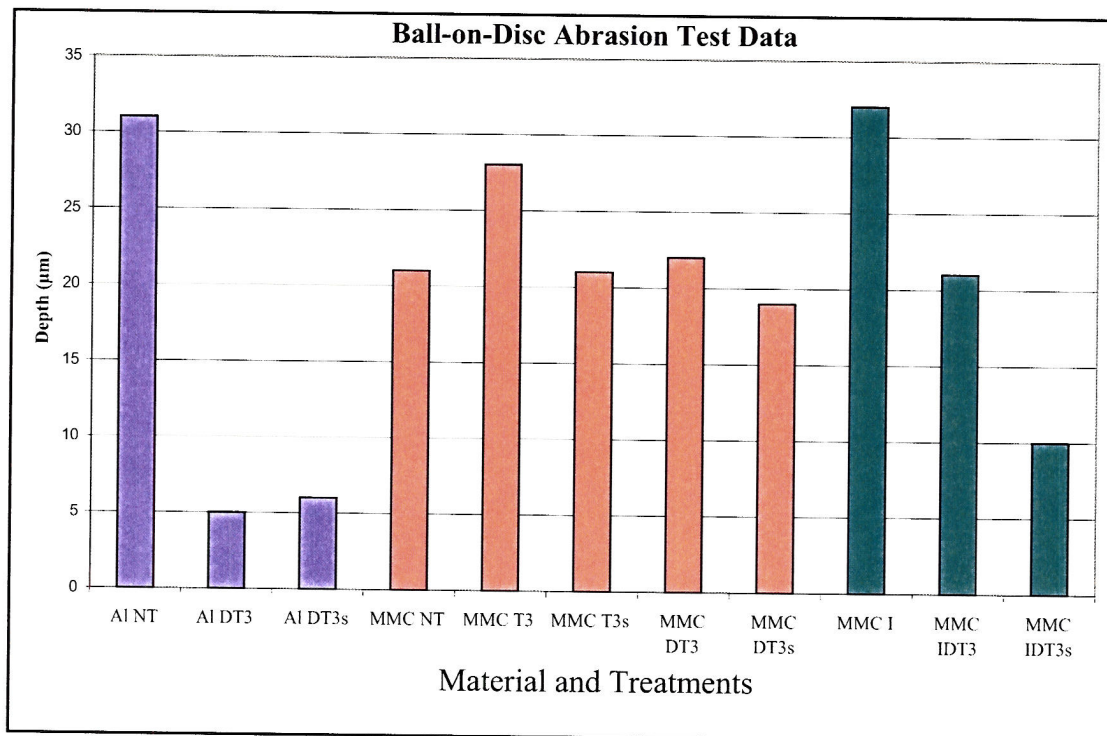


Figure 11. Depth of groove measurements from 1000-m distance of ball-on-disc wear testing. Refer to table 1 for sample preparation and identification.

No clear trend was observed for wear resistance of anodized MMC. Figure 11 shows that all MMC subjected to the ball-on-disc test performed poorly regardless of whether they were deoxidized prior to anodizing and/or sealed.

The IVD aluminum-coated MMC samples showed incremental improvements in wear resistance when anodized and sealed. Contrary to the monolithic samples, the IVD-coated, anodized, and

sealed samples displayed the best wear resistance of the group. This is likely because the ion vapor deposited aluminum is porous. When anodized, the coating is hardened, but the porosity still exists. By eliminating some of the porosity when the coating is sealed, the wear properties are slightly improved.

4. Summary and Conclusions

The anodic coating formed more uniformly on the monolithic 6061 substrate than on MMC.

1. A sealed anodic coating on MMC provided little corrosion protection beyond the minimum 336 hr of ASTM B 117 salt fog exposure.
2. The anodic coating did not provide improved abrasion resistance to the MMC. However, an aluminum-rich layer applied to the MMC prior to anodizing allowed a more continuous anodic coating to form, thus providing better abrasion protection.
3. Although porous, the anodized IVD aluminum interlayer provided improved corrosion resistance for the MMC samples which demonstrates that an aluminum-rich outer layer is recommended for MMC to achieve performance comparable to an anodic coating on monolithic material.

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